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(54) Title: ADHESION-ENHANCING COATINGS FOR OPTICALLY FUNCTIONAL COATINGS MATERIALS

(57) Abstract

An adhesion-enhancing coating is provided that includes an organic matrix with inorganic oxide particles dispersed therein. The coating is formed from a precursor composition that includes a ceramer composition. A ceramer composition can include at least one ethylenically unsaturated monomer, an optional organofunctional silane monomer coupling agent, and inorganic colloidal particles that at least include silica. An alternative ceramer composition includes an organofunctional silane monomer coupling agent and inorganic colloidal particles that at least include silica.

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ADHESION-ENHANCING COATINGS FOR OPTICALLY FUNCTIONAL COATINGS MATERIALS

Background of the Invention

Optically functional coatings are coatings whose primary function is to either enhance or reduce light reflectance from the surface of transparent substrates, including plastic and glass substrates. When an optically functional coating reduces the amount of light reflected by the plastic or glass substrate, it is called "antireflective." On the other hand, when the optically functional coating enhances the amount of light reflected by the substrate, it is called "reflective." An optically functional coating can be formed from a wide variety of conventional materials.

As described in Optical Thin Film User's Handbook by James D. Rancourt, MacMillan Publishing Co., 1987, optically functional coatings may be formed from suitably deposited thin films of metals (including metalloids) or alloys thereof, such as silver, gold, aluminum, palladium, and palladium-gold. However, one of the most versatile classes of materials used in the deposition of optically functional coatings are metal oxides. Herein, "metal oxides" includes oxides of single metals (including metalloids) as well as oxides of alloys thereof. Examples of particular metal oxides that have been used in optical coatings include oxides of aluminum, silicon, tin, titanium, niobium, zinc, zirconium, tantalum, yttrium, cerium, tungsten, bismuth, indium, and mixtures thereof, such as Al_2O_3, SiO_2, SnO_2, TiO_2, Nb_2O_5, ZnO, ZrO_2, Ta_2O_5, Y_2O_3, CeO_2, WO_3, Bi_2O_5, In_2O_3, and ITO (indium tin oxide). Metal oxides that are depleted in oxygen (that is, where the amount of oxygen in the oxide is less than the stoichiometric amount), such as SiO_x, where x is no greater than 2, have also been used. One method of synthesizing such oxygen deficient oxides is by a modified sputtering technique called reactive sputtering. One of the reasons for the versatility of metal oxides in optically functional coatings is the fact that unlike other materials, they may be

used to deposit both reflective or antireflective coatings depending on the configuration of the oxide coating and its chemical composition. Thus, as discussed in International Publication Document WO 96/31343 (Bright), when a single thin layer of metal oxide, such as ITO, having a thickness of about 50 Angstroms to about 3000 Angstroms is deposited over a transparent plastic film, such as polyester or polycarbonate, the amount of light reflected by the polyester or polycarbonate increases substantially. In this case the ITO film acts as a "reflective" coating. On the other hand, when alternating layers of ITO and SiO_2 or ITO and SiO_x with a combined thickness of about 50 Angstroms to about and 3000 Angstroms are deposited over the polyester or polycarbonate substrate, the amount of light reflected by the polyester or polycarbonate decreases substantially. In this case the alternating ITO/SiO_x stack acts as an "antireflective" coating. Another reason for the versatility of metal oxide coatings, particularly ITO, is that they can be made electrically conductive by doping them with conductive elements, such as tin, aluminum, barium, boron, and antimony. When made conductive, the metal oxides also help reduce static charge and electromagnetic emissions.

Whether an optically functional coating is "reflective" or "antireflective" depends on its overall refractive index relative to the refractive index of the underlying substrate. The simplest reflective coating is a single thin layer of a transparent material, such as a metal or metal oxide, having a refractive index higher than the refractive index of the underlying substrate. Thus, when the substrate is a transparent organic polymeric material, such as polyester or polycarbonate, the simplest "reflective" coating is generally chosen to be a single thin layer of a material, such as a metal or metal oxide, having a refractive index of about 1.6 to about 2.7. This is because most organic polymeric materials have indices of refraction of about 1.3 (for fluorinated polymers) to about 1.7 (for aromatic polymers). Fluorinated thermoplastic polymers, such as TEFLON (1.35), have the lowest indices of refraction among organic polymers, whereas aromatic thermoplastic polymers, such as polystyrene (1.60), have some of the highest.

The simplest antireflective coating is a single layer of a transparent material having a refractive index lower than that of the substrate on which it is disposed.

Multilayer antireflective coatings include two or more layers of dielectric material on a substrate, wherein at least one layer has a refractive index higher than the refractive index of the substrate. The multilayer coatings are generally deposited thermal evaporation and sputtering techniques, as well as other vacuum deposition techniques. Such multilayer coatings are disclosed, for example, in International Publication No. WO 96/31343 (Southwall Technologies Inc.), U.S. Pat. Nos. 5,091,244 (Bjornard), 5,105,310 (Dickey), 5,147,125 (Austin), 5,270,858 (Dickey), 5,372,874 (Dickey et al.), 5,407,733 (Dickey), and 5,450,238 (Bjornard et al.)

Antireflective (AR) coatings, in particular, are becoming increasingly important in commercial applications. The transparency of plastic or glass, in the form of doors, windows, lenses, filters, display devices (for example, display panels) of electronic equipment, and the like, can be impaired by glare or reflection of light. To reduce the amount of glare on plastic or glass, the surface typically includes a single layer of a metal oxide (such as silicon dioxide), or suitably alternating multilayers of metal oxides, such as ITO/SiO_2. For example, glass surfaces have about 4% surface reflection, but with the aid of specialized coatings, such as multilayers of sputter deposited ITO/SiO_2, this surface reflection can be reduced to less than about 0.5% in the visible region of the spectrum (400-700 nm). Antireflective (AR) film stacks prepared by vacuum sputtering of metal oxide thin films on substrates made of organic polymeric substrates, particularly flexible plastic substrates, such as polycarbonate, acrylic, polystyrene, and polyesters have been disclosed for example in U.S. Pat. No. 5,579,162 (Bjornard et al.) and International Publication No. WO 96/31343 (Southwall Technologies Inc.).

While sputter deposited metal oxide thin films generally adhere very well to glass and other inorganic surfaces, their adhesion to polymeric organic surfaces and especially their durability and scratch resistance when deposited directly on these polymeric surfaces are often inferior. This is mainly due to the fact that organic polymeric surfaces, such as the surface of transparent polyester or acrylic films, are themselves very soft and lack the cohesive strength necessary to make them resistant to scratching or other forms of abrasion encountered in everyday use.

Methods for treating organic polymeric substrates to enhance the adhesion of coatings applied thereto are known in the art. For example, methods such as chemical etching, electron-beam irradiation, corona treatment, plasma etching, and coextrusion of adhesion promoting layers are known and discussed, for example, in the Handbook of Adhesion, edited by D.E. Packham, John Wiley & Sons, New York (1992). None of these methods, however, result in a significant increase in the hardness or scratch resistance of the organic polymeric surface. One method disclosed in U.S. Pat. No. 5,639,546 (Bilkadi) involves the use of a primer layer containing the cured product of polyethylenically unsaturated monomers and an inorganic oxide sol to enhance adhesion of an organic material to an organic polymeric substrate. However, there is still a need for enhancing the adhesion of optically functional coatings, particularly antireflective coatings, to organic polymeric substrates, particularly flexible organic polymeric substrates.

Summary of the Invention

Thus, the present invention provides an adhesion-enhancing coating for use on organic polymeric substrates that is sufficiently scratch resistant while providing an adherent surface for the application of an optically functional coating. The present invention provides a precursor composition curable to an adhesion-enhancing coating for organic polymeric substrates, particularly, thermoplastic transparent substrates useful in optical applications. Once applied to a polymeric substrate, the precursor compositions cure (or at least partially cure) to glass-like materials that impart superior hardness, scratch resistance, and adhesion properties to optically functional coatings, such as antireflective coatings (for example, indium tin oxide), that are subsequently applied thereto. Advantageously, by including an adhesion-enhancing coating on an organic polymeric substrate formed from the precursor composition, the coated substrate is a more durable substrate for use in CRT screens, television screens, corrective lenses, prisms, mirrors, energy control windows and windshields, and the like.

The adhesion-enhancing coating includes an organic matrix with inorganic oxide particles dispersed therein. The adhesion-enhancing precursor composition includes a ceramer composition and one or more optional organic solvents. A ceramer composition includes an organic polymeric binder material curable to the

organic matrix with colloidal inorganic oxide particles dispersed therein. In one embodiment, a ceramer composition in accordance with the present invention includes at least one ethylenically unsaturated monomer, an optional organofunctional silane monomer coupling agent, and inorganic colloidal particles that at least include silica. An alternative ceramer composition according to the present invention includes an organofunctional silane monomer coupling agent and inorganic colloidal particles that at least include silica.

As used herein with respect to the present invention, the following shall apply:

"Ceramer composition" refers to a coatable dispersion comprising substantially non-aggregated, colloidal inorganic oxide particles dispersed in a curable organic binder composition, wherein curing of the binder is understood to mean in a broad sense the process of solidification (hardening) of the binder brought about by a suitable approach such as cooling of a molten thermoplastic material, drying of a solvent-containing composition, chemical crosslinking of a thermosetting composition, radiation curing of a radiation curable composition, or the like;

"Ceramer coating" refers to a coating of a ceramer composition in which the curable composition is cured to form a solid, substantially non-flowing material; and

"Curable" means that a coatable material can be transformed into a solid, substantially non-flowing material by means of cooling (to solidity hot melts), heating (to dry and solidify materials in a solvent), chemical crosslinking, radiation crosslinking, or the like.

During the manufacture of the coated organic polymeric substrate, the precursor composition is applied to at least a portion of the organic polymeric substrate. Preferably and advantageously, this precursor composition is directly applied to the organic polymeric substrate. Optionally, the precursor composition can be applied to the organic polymeric substrate that has been primed, for example treated with a conventional primer such as an acrylic latex.

The adhesion-enhancing ceramer composition is in a flowable state, which is subsequently exposed to conditions, preferably an energy source, that cure the

composition and form an adhesion-enhancing coating. The conditions that affect curing include thermal energy, electron beam, ultraviolet light, or visible light.

The present invention provides a composite structure comprising an organic polymeric substrate having a first surface and a second surface; an adhesion-enhancing coating on the first surface, wherein the coating comprises an organic matrix having inorganic oxide particles dispersed therein; wherein the organic matrix comprises at least one polymerized ethylenically unsaturated monomer and the inorganic oxide particles comprise silica particles; and an optically functional coating on the adhesion-enhancing coating. Preferably, the adhesion-enhancing coating is prepared from a ceramer composition comprising at least one ethylenically unsaturated monomer, colloidal inorganic oxide particles that include at least silica particles, and an optional organofunctional silane monomer coupling agent.

The ethylenically unsaturated monomer is selected from the group of a monofunctional ethylenically unsaturated monomer, a multifunctional ethylenically unsaturated monomer, and a combination thereof. Preferably, the monofunctional ethylenically unsaturated monomer is selected from the group of a monofunctional (meth)acrylic acid ester, a (meth)acrylamide, an alpha-olefin, a vinyl ether, a vinyl ester, and a combination thereof. Preferably, the multifunctional monomer is a multifunctional unsaturated ester of (meth)acrylic acid of the formula:

$$\left[H_2C{=}\underset{\displaystyle R^4}{\underset{|}{C}}{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}O \right]_m{-}R^5{-}Y_n$$

wherein R^4 is hydrogen, halogen or a (C_1-C_4)alkyl group; R^5 is a polyvalent organic group selected from the group of a cyclic, a branched, a linear, an aliphatic, an aromatic, or a heterocyclic moiety having carbon, hydrogen, nitrogen, nonperoxidic oxygen, sulfur, or phosphorus atom; Y is hydrogen, (C_1-C_4)alkyl, or a protic functional group selected from the group consisting of -OH, -COOH, -SH, -$PO(OH)_2$, -SO_3H, and -$SO(OH)_2$; m is an integer of at least 2; and n is an integer having a value of 1 to 3.

In an alternative embodiment, the present invention provides an antireflective composite structure comprising an organic polymeric substrate having a first surface and a second surface; an adhesion-enhancing coating on the first surface, wherein the coating comprises an organic matrix and inorganic colloidal particles that at least include silica dispersed in the organic matrix; and an antireflective coating on the adhesion-enhancing coating. The antireflective coating is preferably substantially hydrocarbon free. More preferably, the antireflective coating comprises at least one film comprising a material selected from the group of oxides of aluminum, silicon, tin, titanium, niobium, zinc, zirconium, tantalum, yttrium, aluminum, cerium, tungsten, bismuth, indium, and mixtures thereof.

The present invention also provides an optically functional structure comprising an organic polymeric substrate having a first surface and a second surface; an adhesion-enhancing coating on the first surface wherein the coating comprises an organic matrix and inorganic colloidal particles that at least include silica dispersed in the organic matrix; wherein the organic matrix is formed from an adhesion-enhancing precursor composition comprising a ceramer composition comprising an organofunctional silane monomer coupling agent, and colloidal inorganic oxide particles that at least include silica; and an optically functional coating on the adhesion-enhancing coating, wherein the optically functional coating is substantially carbon free. Methods of forming such structures are also provided.

Detailed Description of Preferred Embodiments

Preferably, transparent articles in accordance with the present invention include coatings of one or more layers of at least one optically functional material deposited on a transparent (that is, light transmissive) organic polymeric substrate. An adhesion-enhancing coating according to the present invention is used to enhance adhesion of an optically functional layer or stack to an organic polymeric substrate. Additionally, and advantageously, the adhesion-enhancing coating for an organic polymeric substrate of the present invention also imparts glass-like properties to the substrate, such as scratch resistance. Thus, an adhesion-enhancing coating should not significantly degrade the organic polymeric substrate or

adversely affect its physical properties. An adhesion-enhancing coating should also adhere well to an organic polymeric substrate, particularly a thermoplastic material.

Optically functional materials, which when deposited or coated on a transparent substrate, alter the reflective properties of the substrate, as discussed above. That is, an optically functional material may provide a reflective or mirror-like property to the substrate or it may provide an antireflective property.

The optically functional coating can be formed from a wide variety of conventional materials as discussed above. For certain embodiments of the present invention, optically functional materials are preferably substantially hydrocarbon free. As used herein, "hydrocarbon" refers to a group or moiety that generally contains only carbon and hydrogen and is typically classified as an aliphatic group, a cyclic group, or a combination of aliphatic and cyclic groups (for example, alkaryl and aralkyl groups). This term does not refer to carbon coatings, such as diamond-like carbon coatings. However, for certain embodiments of the present invention, optically functional materials are preferably substantially carbon free.

An optically functional coating for use in the present invention can be formed from a wide variety of conventional materials. They can include metals or metal alloys, such as silver, gold, aluminum, palladium, and palladium-gold, metal oxides such as oxides of aluminum, silicon, tin, titanium, niobium, zinc, zirconium, tantalum, yttrium, aluminum, cerium, tungsten, bismuth, indium, and mixtures thereof (for example, Al_2O_3, SiO_x, particularly SiO_2, SnO_2, TiO_2, Nb_2O_5, ZnO, ZrO_2, Ta_2O_5, Y_2O_3, Al_2O_3, CeO_2, WO_3, Bi_2O_5, In_2O_3, and ITO (indium tin oxide)), or carbon as in diamond-like carbon coatings. As used herein, "metals," "metal alloys," and "metal oxides" include both metals and metalloids.

Preferably, the optically functional coating is an antireflective coating, which can be in the form of a single layer of a transparent material, or two or more layers of dielectric material on a substrate. More preferably, the antireflective coating includes one or more metal oxides in one or more layers. Most preferably, the metal oxides are vacuum deposited, particularly, sputter coated. A particularly preferred antireflective coating includes alternating layers of ITO and SiO_x

(typically, SiO_2) or with SiO_x as the outermost layer and ITO as the layer directly contacting the adhesion-enhancing coating.

Representative organic polymeric substrates include transparent polyesters, such as poly(ethyleneterephthalate) "PET", polycarbonates, poly(meth)acrylates, polyphenyleneoxide, cellulose esters, such as cellulose acetate and cellulose acetate-butyrate copolymer "CAB", polystyrene and styrene copolymers such as acrylonitrile-butadiene-styrene copolymer and acrylonitrile-styrene copolymer, polyolefins, such as polypropylene and polyethylene, polyvinyl chloride, polyimides, and the like. Other polymers (including copolymers, terpolymers, etc.) which have indices of refraction below that of an antireflective coating may be used. The term "poly(meth)acrylate" includes acrylates and methacrylates commonly referred to as cast acrylic sheeting, stretched acrylic, poly(methylmethacrylate) "PMMA," poly(methacrylate), poly(ethylacrylate), and poly(methylmethacrylate-co-ethylacrylate), and the like. Preferably, the thermoplastic substrates to which the coatings of the present invention adhere the most effectively are made from optically transmissive thermoplastic materials (that is, plastic sheets, films, or bodies having integrated transmissions over the visible wavelengths of at least 25% to about 90% without marked absorption or reflection peaks in this range) such as polyethylene terephthalate, "PET", polymethyl methacrylate, polycarbonate, polystyrene, and cellulose acetate. The substrate thickness can vary, however, it typically ranges from about 0.1 mm to about 1000 mm, and more typically from about 10 mm to about 200 mm. Flexible organic film substrates, however, are typically no greater than about 1 mm thick. Additionally, the organic polymeric substrate can be a laminate of two or more different thermoplastic materials adhered together, either with or without an adhesive layer therebetween. The organic polymeric substrate can be made by a variety of different methods. For example, the thermoplastic material can be extruded and then cut to the desired dimension. It can be molded to form the desired shape and dimension. Also, it can be cell cast and subsequently heated and stretched to form the organic polymeric substrate.

The organic polymeric substrate on which the optically functional coating is applied may include a primed surface, which can be provided by a chemical primer

layer or by other methods such as chemical etching, electron-beam irradiation, corona treatment, plasma etching, or coextrusion of adhesion promoting layers. Flexible organic polymeric substrates that contain primed surfaces are commercially available. An example of such a material is a polyethylene terephthalate film primed with an aqueous acrylic latex, which is available from Imperial Chemical Industries, Hopewell, VA, under the trade designation ICI 617. Preferably, the organic polymeric substrate is primed for enhanced adhesion of the adhesion-enhancing coating to the substrate.

During manufacture, an adhesion-enhancing precursor composition is applied to at least one surface of the organic polymeric substrate and at least partially cured to form the adhesion-enhancing coating. The curing process can be carried out at room temperature (typically, about 20°C to about 25°C) with UV or e-beam radiation, for example, which is particularly advantageous for substrates that warp during the thermal curing of coatings. The adhesion-enhancing coating is applied to the outer surface of the organic polymeric substrate as a liquid, flowable ceramer composition. Upon curing, that is, polymerizing and/or crosslinking, the ceramer composition is solidified to form a coating, sometimes referred to as a "hard coat."

The adhesion-enhancing precursor composition includes a ceramer composition and one or more optional solvents. The ceramer composition includes substantially non-aggregated, colloidal inorganic oxide particles dispersed in a curable organic binder composition. Preferably, the ceramer composition has a refractive index of about 1.40 to about 1.65, as measured with a conventional refractometer using a conventional measurement procedure, such as ASTM D1747-94 ("Standard Test Method for Refractive Index of Viscous Materials"). Preferably, the curable organic binder of the ceramer composition has a refractive index of about 1.40 to about 1.60. Preferably, the cured adhesion-enhancing coating has a refractive index of about 1.45 to about 1.70, and more preferably, about 1.50 to about 1.65.

The curable organic binder of the ceramer composition can include a variety of monomers, oligomers, and/or polymers that can form a cured matrix for inorganic oxide particles. Preferably, ceramer compositions in accordance with the

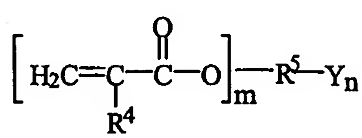
present invention include an ethylenically unsaturated monomer, an optional organofunctional silane monomer coupling agent, and inorganic colloidal particles that at least include silica. An alternative ceramer composition in accordance with the present invention is made from an organofunctional silane monomer coupling agent and inorganic colloidal particles that at least include silica.

Ethylenically Unsaturated Monomer

Preferably, the ethylenically unsaturated is a monofunctional ethylenically unsaturated monomer or a multifunctional ethylenically unsaturated monomer, or a combination thereof. Preferably, each of the monomers has a refractive index of about 1.40 to about 1.65.

The multifunctional ethylenically unsaturated monomer is preferably an ester of (meth)acrylic acid. It is more preferably selected from the group consisting of a difunctional ethylenically unsaturated ester of acrylic or methacrylic acid, a trifunctional ethylenically unsaturated ester of acrylic or methacrylic acid, a tetrafunctional ethylenically unsaturated ester of acrylic or methacrylic acid, and a combination thereof. Of these, trifunctional and tetrafunctional ethylenically unsaturated esters of (meth)acrylic acid are more preferred.

Preferred multifunctional ethylenically unsaturated esters of (meth)acrylic acid have a refractive index of about 1.40 to about 1.65 and can be described by the formula:



wherein R^4 is hydrogen, halogen or a $(C_1\text{-}C_4)$alkyl group (preferably R^4 is hydrogen or a methyl group); R^5 is a polyvalent organic group, which can be cyclic, branched, or linear, aliphatic, aromatic, or heterocyclic, having carbon, hydrogen, nitrogen, nonperoxidic oxygen, sulfur, or phosphorus atoms; Y is hydrogen, $(C_1\text{-}C_4)$alkyl, or a protic functional group; m is an integer designating the number of acrylic or methacrylic groups in the ester and has a value of at least 2; and n has a value of the valence of R^5 - m. Referring to this formula, preferably, R^5 has a molecular weight of about 14-100, m has a value of 2-6 (more preferably m has a

value of 2-5, most preferably m has a value of 3-4, or where a mixture of multifunctional acrylates and/or methacrylates are used, m has an average value of about 2.05-5), and n is an integer having a value of 1 to 3. Preferred protic functional groups are selected from the group consisting of -OH, -COOH, -SH, -$PO(OH)_2$, -SO_3H, and -$SO(OH)_2$.

Examples of suitable multifunctional ethylenically unsaturated esters of (meth)acrylic acid are the polyacrylic acid or polymethacrylic acid esters of polyhydric alcohols including, for example, the diacrylic acid and dimethylacrylic acid ester of aliphatic diols such as ethyleneglycol, triethyleneglycol, 2,2-dimethyl-1,3-propanediol, 1,3-cyclopentanediol, 1-ethoxy-2,3-propanediol, 2-methyl-2,4-pentanediol, 1,4-cyclohexanediol, 1,6-hexamethylenediol, 1,2-cyclohexanediol, 1,6-cyclohexanedimethanol; the triacrylic acid and trimethacrylic acid esters of aliphatic triols such as glycerin, 1,2,3-propanetrimethanol, 1,2,4-butanetriol, 1,2,5-pentanetriol, 1,3,6-hexanetriol, and 1,5,10-decanetriol; the triacrylic acid and trimethacrylic acid esters of tris(hydroxyethyl) isocyanurate; the tetraacrylic and tetramethacrylic acid esters of aliphatic triols, such as 1,2,3,4-butanetetrol, 1,1,2,2,-tetramethylolethane, 1,1,3,3-tetramethylolpropane, and pentaerythritol tetraacrylate; the pentaacrylic acid and pentamethacrylic acid esters of aliphatic pentols such as adonitol; the hexaacrylic acid and hexamethacrylic acid esters of hexanols such as sorbitol and dipentaerythritol; the diacrylic acid and dimethacrylic acid esters of aromatic diols such as resorcinol, pyrocatechol, bisphenol A, and bis(2-hydroxyethyl) phthalate; the trimethacrylic acid ester of aromatic triols such as pyrogallol, phloroglucinol, and 2-phenyl-2,2-methylolethanol; and the hexaacrylic acid and hexamethacrylic acid esters of dihydroxy ethyl hydantoin; and mixtures thereof.

Preferably, the multifunctional ethylenically unsaturated ester of (meth)acrylic acid is a nonpolyethereal multifunctional ethylenically unsaturated ester of (meth)acrylic acid. More preferably, the multifunctional ethylenically unsaturated ester of (meth)acrylic acid is selected from the group consisting of pentaerythritol triacrylate (PETA), pentaerythritol trimethacrylate, and a combination thereof. Most preferably, the multifunctional ethylenically unsaturated ester of (meth)acrylic acid is pentaerythritol triacrylate.

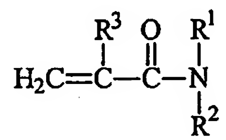
In addition to the multifunctional ethylenically unsaturated esters of acrylic acid, the ceramer composition can include a monofunctional ethylenically unsaturated esters of (meth)acrylic acid (that is, an alkyl and/or aryl acrylate or methacrylate). Preferably, the alkyl group of the (meth)acrylate has about 4 to about 14 carbon atoms (on average). The alkyl group can optionally contain oxygen atoms in the chain thereby forming ethers, for example. Preferably, the aryl group of the (meth)acrylate has about 6 to about 20 carbon atoms (on average).

Examples include, but are not limited to, 2-hydroxyethyl acrylate, 2-hydroxymethyl acrylate, 2-methylbutyl acrylate, isooctyl acrylate, lauryl acrylate, 4-methyl-2-pentyl acrylate, isoamyl acrylate, sec-butyl acrylate, n-butyl acrylate, n-hexyl acrylate, 2-ethylhexyl acrylate, n-octyl acrylate, n-decyl acrylate, isodecyl acrylate, isodecyl methacrylate, and isononyl acrylate. Other examples include, but are not limited to, poly-ethoxylated or -propoxylated methoxy (meth)acrylate (that is, poly(ethylene/propylene oxide) mono-(meth)acrylate) macromers (that is, macromolecular monomers), polymethylvinyl ether mono(meth)acrylate macromers, and ethoxylated or propoxylated nonyl-phenol acrylate macromers. The molecular weight of such macromers (that is, macromolecular monomers) is typically about 100 grams/mole to about 600 grams/mole, and preferably, about 300 grams/mole to about 600 grams/mole. Preferred monofunctional (meth)acrylates that can be used include 2-methylbutyl acrylate, isooctyl acrylate, lauryl acrylate, and methoxy-capped poly(ethylene glycol) mono-methacrylate.

The monofunctional ethylenically unsaturated monomer may also be selected from the group of a (meth)acrylamide, an alpha-olefin, a vinyl ether, a vinyl ester, and a combination thereof. Examples include, but are not limited to, acrylamides, such as acrylamide, methacrylamide, N-methyl acrylamide, N-ethyl acrylamide, N-methylol acrylamide, N-hydroxyethyl acrylamide, diacetone acrylamide, N,N-dimethyl acrylamide, N,N-diethyl acrylamide, N-ethyl-N-aminoethyl acrylamide, N-ethyl-N-hydroxyethyl acrylamide, N,N-dimethylol acrylamide, N,N-dihydroxyethyl acrylamide, t-butyl acrylamide, dimethylaminoethyl acrylamide, N-octyl acrylamide (normal and branched), and 1,1,3,3-tetramethylbutyl acrylamide. Other examples include acrylic acid, methacrylic acid, itaconic acid, crotonic acid, maleic acid, fumaric acid, 2,2'-

(ethoxyethoxy)ethyl acrylate, 2-hydroxyethyl acrylate or methacrylate, 2-hydroxypropyl acrylate or methacrylate, 3-hydroxypropyl acrylate or methacrylate, t-butyl acrylate, n-butyl methacrylate, isobornyl acrylate, 2-(phenoxy)ethyl acrylate or methacrylate, biphenylyl acrylate, t-butylphenyl acrylate, cyclohexyl acrylate, dimethyladamantyl acrylate, 2-naphthyl acrylate, phenyl acrylate, N-vinyl pyrrolidone, and N-vinyl caprolactam. Preferred reinforcing monofunctional acrylic monomers include acrylic acid, t-butyl acrylate, N,N-dimethyl acrylamide, 1,1,3,3-tetramethylbutyl acrylamide, N-octyl acrylamide, 2-(phenoxy) ethyl acrylate, 2-hydroxypropyl acrylate, 3-hydroxypropyl acrylate, isobornyl acrylate, and 2-(phenoxy)ethyl acrylate.

In general, the acrylamide compounds have the following formula:



wherein: R^1 and R^2 are each independently hydrogen, a $(C_1\text{-}C_8)$alkyl group optionally having hydroxy, halide, carbonyl, and amido functionalities, a $(C_1\text{-}C_8)$alkylene group optionally having carbonyl and amido functionalities, a $(C_1\text{-}C_4)$alkoxymethyl group, a $(C_4\text{-}C_{18})$aryl group, a $(C_1\text{-}C_3)$alk$(C_4\text{-}C_{18})$aryl group, and a $(C_4\text{-}C_{18})$heteroaryl group; with the proviso that only one of R^1 and R^2 is hydrogen; and R^3 is hydrogen, a halogen, or a methyl group. Preferably, R^1 is a $(C_1\text{-}C_4)$alkyl group; R^2 is a $(C_1\text{-}C_4)$alkyl group; and R^3 is hydrogen, a halogen, or a methyl group. R^1 and R^2 can be the same or different. More preferably, each of R^1 and R^2 is CH_3, and R^3 is hydrogen.

Examples of suitable acrylamides are N-(3-bromopropionamidomethyl)acrylamide, N-tert-butylacrylamide, N,N-dimethylacrylamide, N,N-diethylacrylamide, N-(5,5-dimethylhexyl)acrylamide, N-(1,1-dimethyl-3-oxobutyl)acrylamide, N-(hydroxymethyl)acrylamide, N-(isobutoxymethyl)acrylamide, N-isopropylacrylamide, N-methylacrylamide, N-ethylacrylamide, N-methyl-N-ethylacrylamide, N-(fluoren-2-yl)acrylamide, N-(2-fluorenyl)-2-methylacrylamide, 2,3-bis(2-furyl)acrylamide, N,N'-methylene-bis acrylamide. A particularly preferred acrylamide is N,N-dimethyl acrylamide.

Optional Organofunctional Silane Monomer Coupling Agent

A wide variety of organofunctional silane monomers may be used in the practice of the present invention. The preferred organofunctional silanes are hydrolyzable organofunctional silanes, also known in the art as "coupling agents" for coupling silica particles to organic materials. Representative examples include methyl trimethoxysilane, methyl triethoxysilane, phenyl trimethoxysilane, phenyl triethoxysilane, (meth)acryloxyalkyl trimethoxysilanes, such as methacryloxypropyl trimethoxysilane, (meth)acryloxypropyl trichlorosilane, phenyl trichlorosilane, vinyl trimethoxysilane, vinyl triethoxysilane, propyl trimethoxysilane, propyl triethoxysilane, glycidoxypropyl trimethoxysilane, glycidoxypropyl triethoxysilane, glycidoxypropyl trichlorosilane, perfluoro alkyl trimethoxysilane, perfluoro alkyl triethoxysilane, perfluoromethyl alkyl trimethoxysilanes, such as tridecafluoro-1,1,2,2 tetrahydrooctyl trimethoxysilane, perfluoroalkyl trichlorosilanes, trifluoromethylpropyl trimethoxysilane, trifluoromethylpropyl trichlorosilane, and perfluorinated sulfonimido ethyl trimethoxysilane (available from the Minnesota Mining and Manufacturing Company, St. Paul, MN, under the trade designation FC 405), combinations of these, and the like. Optionally, the colloidal inorganic particles may be surface treated with a silane coupling agent and, in such embodiments, the coupling agent may be the same or different from the silane monomers used to form the bulk of the organic binder of the ceramer composition.

Colloidal Inorganic Particles

In the present invention, a ceramer composition includes colloidal inorganic particles that at least include silica. Silica sols useful for preparing ceramer compositions can be prepared by methods well known in the art. A used herein, "sol" shall refer to a colloidal dispersion of substantially non-aggregated, inorganic oxide particles in a liquid medium. Colloidal silicas dispersed as sols in aqueous solutions are also available commercially under such trade names as LUDOX (E.I. DuPont de Nemours and Co., Wilmington, DE), NYACOL (Nyacol Co., Ashland, MA), and NALCO (Nalco Chemical Co., Oak Brook, IL). Nonaqueous silica sols (also called silica organosols) are also commercially available under the trade names NALCO 1057 (a silica sol in 2-propoxyethanol, Nalco Chemical Co.) and

MA-ST, IP-ST, and EG-ST (Nissan Chemical Ind., Tokyo, Japan). The silica particles preferably have an average particle diameter of about 5 nm to about 1000 nm, and more preferably, about 10 nm to about 50 nm. Average particle size can be measured using transmission electron microscopy to count the number of particles of a given diameter. Additional examples of suitable colloidal silicas are described in U.S. Pat. No. 5,126,394 (Bilkadi).

Preferably, the silica particles are functionalized with a coupling agent. More preferably, the silica particles are (meth)acrylate functionalized. Herein, "(meth)acrylate functionalized" means the silica particles are functionalized with a (meth)acrylate terminated organofunctional silane. The functionalized particles bond intimately and isotropically with the organic matrix. Typically, the silica particles are functionalized by adding a (meth)acrylate functionalized silane to aqueous colloidal silica. Examples of (meth)acrylate functionalized colloidal silica are described in U.S. Pat. Nos. 4,491,508 (Olsen et al.), 4,455,205 (Olsen et al.), 4,478,876 (Chung), 4,486,504 (Chung), and 5,258,225 (Katsamberis).

In addition to silica, the colloidal inorganic particles may further include colloidal particles of higher refractive index than silica. Examples of such higher index colloidal particles include, but are not limited to, alumina, titania, zirconia, ceria, and antimony oxide sols, all of which are available commercially from suppliers such as Nyacol Co., Ashland, MA, and Nalco Chemical Co., Oak Brook, IL.

It is highly desirable that the colloidal inorganic particles of the coating be derived from a sol rather than a powder, which can result in an intractable mass that is unsuitable for coating as an aqueous sol. The addition of additives, such as high molecular weight polymers, may enable compositions derived from colloidal powder to be cast on to inorganic polymeric substrates. However, it is believed that the use of compositions containing colloidal powder will result in coatings having relatively poor optical transparency and poor flow properties for coating. Therefore, the use of colloidal powders is not preferable in the coatings of the present invention. The colloidal silica particles are employed in the coating at 10% to 50% by weight, and more preferably, at 25% to 40% by weight, and most preferably, at 30% to 33% by weight.

A ceramer composition of the present invention preferably includes an organic matrix and colloidal inorganic particles that at least include silica. Preferably, the organic matrix is prepared from a curable organic binder that includes an ethylenically unsaturated monomer selected from the group of a multifunctional ethylenically unsaturated ester of (meth)acrylic acid, a monofunctional ethylenically unsaturated monomer (for example, an ester or amide), and a combinations thereof; and an optional organofunctional silane coupling agent.

The ceramer composition preferably includes no greater than about 80 percent by weight (wt.%) of at least one ethylenically unsaturated monomer and at least about 20 wt.% colloidal inorganic oxide particles, based on the total weight of the ceramer composition. Preferably, it includes at least about 40 wt.% of at least one ethylenically unsaturated monomer, and no greater than about 60 wt.% of colloidal inorganic oxide particles.

If the ethylenically unsaturated monomers used include a mixture of multifunctional and monofunctional ethylenically unsaturated monomers, the multifunctional monomer is preferably used in an amount of at least about 20 wt.%, and the monofunctional monomer is preferably used in an amount of at least about 5 wt.%. Preferably, the multifunctional monomer is used in an amount of no greater than about 60 wt.%, and the monofunctional monomer is used in an amount of no greater than about 20 wt.%.

If used, an organofunctional silane coupling agent is preferably used in an amount of no greater than about 80 wt.%, more preferably, no greater than about 70 wt.%, and most preferably, no greater than about 60 wt.%, based on the total weight of the ceramer composition. It is preferably used in an amount of at least about 5 wt.%, more preferably, at least about 10 wt.%, and most preferably, at least about 20 wt.%, based on the total weight of the ceramer composition.

It is the combination of the organic matrix with the colloidal inorganic oxide particles that at least include silica (with or without a coupling agent) that results in unexpected and improved properties as a adhesion-enhancing coating. The multifunctional ethylenically unsaturated esters of (meth)acrylic acid tend to increase the hardness of the coating, whereas the monofunctional ethylenically

unsaturated monomer tends to "toughen" the coating without significant loss in abrasion resistance. This toughness property also results in the coating being able to be flexed.

In many instances, the adhesion-enhancing coating can adhere directly to the organic polymeric substrate without the need for an additional primer or adhesion promoter, which is advantageous at least because this results in a labor and material savings.

<u>**Initiators and Photosensitizers**</u>

During the manufacture of an abrasion resistant coating, the ceramer composition is exposed to an energy source, for example, heat or UV or e-beam radiation, that initiates the curing process of the ceramer composition. This curing process typically occurs via a free radical mechanism, which can require the use of a free radical initiator (simply referred to herein as an initiator, for example, a photoinitiator or a thermal initiator). If the energy source is an electron beam, the electron beam generates free radicals and no initiator is required. If the energy source is heat, ultraviolet light, or visible light, an initiator is required. When the initiator is exposed to one of these energy sources, the initiator generates free radicals, which then initiates the polymerization and crosslinking.

Examples of suitable free radical thermal initiators include, but are not limited to, peroxides such as benzoyl peroxide, azo compounds, benzophenones, and quinones. Examples of photoinitiators that generate a free radical source when exposed to visible light radiation include, but are not limited to, benzophenones. Examples of photoinitiators that generate a free radical source when exposed to ultraviolet light include, but are not limited to, organic peroxides, azo compounds, quinones, benzophenones, nitroso compounds, acryl halides, hydrozones, mercapto compounds, pyrylium compounds, triacrylimidazoles, bisimidazoles, chloroalkytriazines, benzoin, benzoin methyl ether, benzoin ethyl ether, benzoin isopropyl ether, benzoin isobutyl ethers and methylbenzoin, diketones such as benzil and diacetyl, phenones such as acetophenone, 2,2,2-tri-bromo-1-phenylethanone, 2,2-diethoxyacetophenone, 2,2-dimethoxy-2-phenylacetophenone, 2,2,2,-tribromo-1(2-nitrophenyl) ethanone, benzophenone, and 4,4-bis(dimethyamino)benzophenone. Examples of commercially available ultraviolet

photoinitiators include those available under the trade designations IRGACURE 184 (1-hydroxycyclohexyl phenyl ketone), IRGACURE 361 and DAROCUR 1173 (2-hydroxy-2-methyl-1-phenyl-propan-1-one) from Ciba-Geigy, Hawthorn, NY. Typically, if used, an amount of an initiator is included in the precursor composition to effect the desired level and rate of cure. Preferably, the initiator is used in an amount of about 0.1 wt.% to about 10 wt.%, and more preferably about 2 wt.% to about 4 wt.%, based on the total weight of the ceramer composition without solvent. It should be understood that combinations of different initiators can be used if desired.

In addition to the initiator, the ceramer composition of the present invention can include a photosensitizer. The photosensitizer aids in the formation of free radicals that initiate curing of the precursor composition, especially in an air atmosphere. Suitable photosensitizers include, but are not limited to, aromatic ketones and tertiary amines. Suitable aromatic ketones include, but are not limited to, benzophenone, acetophenone, benzil, benzaldehyde, and o-chlorobenzaldehyde, xanthone, tioxanthone, 9,10-anthraquinone, and many other aromatic ketones. Suitable tertiary amines include, but are not limited to, methyldiethanolamine, ethyldiethanolamine, triethanolamine, phenylmethyl-ethanolamine, dimethylaminoethylbenzoate, and the like. Typically, if used, an amount of initiator is included in the precursor compositions to effect the desired level and rate of cure. Preferably, the amount of photosensitizer used in the compositions of the present invention is about 0.01 wt.% to about 10 wt.%, more preferably about 0.05 wt.% to about 5 wt.%, and most preferably, about 0.25 wt.% to about 3 wt.%, based on the total weight of the ceramer composition (that is, the adhesion-coating precursor composition without solvent). It should be understood that combinations of different photosensitizers can be used if desired.

Other Optional Additives

The ceramer composition can also preferably include a leveling agent to improve the flow or wetting of the ceramer composition on the transparent thermoplastic substrate. If the ceramer composition does not properly wet the thermoplastic substrate, this can lead to visual imperfections (for example, pin holes and/or ridges) in the coating. Examples of leveling agents include, but are

not limited to, alkoxy terminated polysilicones such as that available under the trade designation DOW 57 (a mixture of dimethyl-, methyl-, and (polyethylene oxide acetate)-capped siloxane) from Dow Corning, Midland, MI; and fluorochemical surfactants such as those available under the trade designations FC430, FC431, and FX313 from Minnesota Mining and Manufacturing Company, St. Paul, MN. The ceramer composition can include an amount of a leveling agent to impart the desired result. Preferably, the leveling agent is present in an amount up to about 3 wt.%, and more preferably, about 0.5 wt.% to about 1 wt.%, based on the total weight of the ceramer composition. It should be understood that combinations of different leveling agents can be used if desired.

Additionally, if organofunctional silane monomers are used, it may be desirable in some instances to add about 1 wt.% to about 3 wt.% glacial acetic acid or similar carboxylic acids as a catalyst for hydrolysis of the organofunctional silane.

Polymeric materials are known to degrade by a variety of mechanisms. Common additives that can offset this are known as stabilizers, absorbers, antioxidants, and the like. The ceramer compositions of the present invention can include one or more of the following: ultraviolet stabilizer, ultraviolet absorber, ozone stabilizer, and thermal stabilizer/antioxidant.

An ultraviolet stabilizer and/or ultraviolet absorber for improving weatherability and reducing the "yellowing" of the adhesion-enhancing coating with time. An example of an ultraviolet stabilizer includes that available under the trade designation TINUVIN 292 (bis(1,2,2,6,6-pentamethyl-4-piperidinyl)sebacate) and an example of an ultraviolet absorber includes that available under the trade designation TINUVIN 1130 (hydroxyphenyl benzotriazole), both of which are available from Ciba-Geigy. The ceramer composition can include an amount of either an ultraviolet stabilizer and/or an ultraviolet absorber to impart the desired result. Preferably, the ultraviolet stabilizer or absorber is present in an amount up to about 10 wt.%, and more preferably, about 1 wt.% to about 5 wt.%, based on the total weight of the ceramer composition. It should be understood that combinations of different ultraviolet stabilizers and absorbers can be used if desired.

An ozone stabilizer protects against degradation resulting from reaction with ozone. Examples of ozone stabilizers include, but are not limited to, hindered amines such as that available under the trade designation IRGONOX 1010 available from Ciba-Geigy and phenoltriazine commercially available from Aldrich Chemical Company, Inc., Milwaukee, WI. The ceramer composition can include an amount of an ozone stabilizer to impart the desired result. Preferably, the ozone stabilizer is present in an amount up to about 1 wt.%, more preferably about 0.1 wt.% to about 1.0 wt.%, and most preferably about 0.3 wt.% to about 0.5 wt.%, based on the total weight of the ceramer composition.

Method of Preparing the Adhesion-Enhancing Coating

The ceramer composition is typically coated out of an organic solvent. Thus, the adhesion-enhancing coating composition typically includes the ceramer composition with one or more organic solvents to reduce the viscosity of the composition and adjust the percent solids content, and thereby enhance the flow characteristics. The desired viscosity depends on various conditions such as the coating thickness, application technique, and the type of substrate. In general, the viscosity of the ceramer composition at 25°C is about 1-200 centipoise, preferably about 3-75 centipoise, more preferably about 4-50 centipoise, and most preferably about 5-20 centipoise. In general, the solids content of the ceramer composition is about 5-99%, preferably about 10-70%, more preferably about 15-30%, and most preferably about 17-26% solids.

The organic solvent should be selected such that it is compatible with the components in the ceramer composition. As used in this context, "compatible" means that there is minimal phase separation between the solvent and the curable organic binder of the ceramer composition. Additionally, the solvent or solvents should be selected such that they do not adversely affect the cured adhesion-enhancing coating properties or attack the thermoplastic material. Furthermore, the solvent(s) should be selected such that they have an appropriate drying rate. That is, the solvent(s) should not dry too slowly, which would slow down the process of making a coated organic polymeric substrate, nor too quickly, which could cause defects such as pin holes or craters in the coating. Examples of suitable solvents include alcohols, preferably the lower alcohols such as isopropyl alcohol, n-

butanol, methanol, ethanol, ketones such as methyl ethyl ketone, glycols, and combinations thereof.

To make the adhesion-enhancing ceramer composition of the invention, all the components are mixed together including the colloidal inorganic particles and the optional organofunctional coupling agent. The mixture is then heated to about 55°C and the solvents (including water) are removed under mild vacuum (about 90 mm Hg) to obtain the ceramer. Additionally, it is preferred to filter the ceramer composition prior to application to a substrate in an effort to remove gel particles or other agglomerated materials. This can be done by filtering the ceramer composition through a ten-, five-, or one-micron filter that is made of a material that is unreactive with the solvent or any of the components of the composition.

The coating can be applied by any technique such as spray coating, knife coating, dip coating, flow coating, roll coating, and the like. In spray coating, the ceramer is atomized and then applied to the outer surface of the substrate. In dip coating, the substrate is immersed into the ceramer and then the excess coating drips off of the substrate. In flow coating, the thermoplastic substrate is held in a vertical position and the ceramer is applied across the top of the substrate. The ceramer then flows down the substrate. In roll coating, the ceramer is applied to the substrate by a roll coater.

A particularly preferred method of coating involves a continuous process. This process includes the steps of placing an organic polymeric substrate having outer surface on a conveyor belt. This substrate is conveyed to a coating station where a ceramer composition is applied to the outer surface. Next, the solvent, if used, is flashed off in a flashing unit, at a temperature suitable for the solvent used. This is typically accomplished at a temperature of about 15-75°C, preferably at a temperature of about 40-65°C. Although a flashing unit is shown, which can be a forced-air oven or an infrared heat source, for example, the solvent can be removed simply by evaporation under ambient conditions. Once the solvent is removed, if it is used, the layer of ceramer composition is exposed to an energy source to initiate curing the ceramer composition to form a adhesion-enhancing coating on the organic polymeric substrate. It should be understood that this is meant to be an

illustration of one process of the invention; it is within the scope of this invention to have many variations on this process.

The ceramer composition should be applied to the organic polymeric substrate in a manner to eliminate or minimize any optical imperfections. If the coating contains defects, such as dust particles or ridges, this can detract from the optical clarity of the transparency or create distortion in the transparency. Some defects can be created during the flashing step; these defects are typically either pin holes or surface roughness caused by uneven drying. To minimize the formation of these defects, the temperature and humidity are often controlled in the clean room or at the coating station. The actual temperature and humidity conditions are dependent upon the chemistry of the ceramer composition. Preferably, the ceramer composition is applied at a temperature of about 15-35°C, and more preferably about 20-25°C. The humidity is preferably about 30-50% relative humidity.

After flashing off the solvent, if used, the ceramer composition is exposed to an energy source to cure the composition and form an adhesion-enhancing (or a hard) coating. This energy source can be thermal energy, electron beam, ultraviolet light, or visible light. The amount of energy required is primarily dependent on the chemistry of the precursor composition, as well as its thickness and density. For thermal energy, the oven temperature will typically range from about 50°C to about 250°C (preferably about 90°C to about 110°C) for about 15 minutes to about 16 hours. It should be noted that care should be taken during thermal curing not to degrade the thermoplastic material. Electron beam radiation can be used at an energy level of about 0.1 megarad to about 10 megarad (Mrad), preferably at an energy level of about 1 Mrad to about 10 Mrad. Ultraviolet radiation refers to nonparticulate radiation having a wavelength within the range of about 200 to about 400 nanometers, preferably within the range of about 250 to 400 nanometers. It is preferred that UV light have an energy level of at least 300 Watts/inch (120 Watts/cm), preferably at least 600 Watts/inch (240 Watts/cm). Visible radiation refers to nonparticulate radiation having a wavelength within the range of about 400 nanometers (nm) to about 800 nm, preferably in the range of about 400 nm to about 550 nm. In general, it is preferred to cure in an inert atmosphere (that is,

minimal oxygen present) such as a nitrogen atmosphere. UV and visible light curing is preferred because there tends to be very little, if any, damage of the thermoplastic material when they are used as the energy source for curing the composition. There is a concern with thermal energy, that if the thermoplastic is either exposed too long and/or at too high of a temperature, this excessive thermal exposure may cause degradation of the thermoplastic material.

The ceramer composition can be applied over the entire substrate surface or a portion thereof. The coating thickness of the ceramer composition will depend upon the formulation and the amount of solvent. Typically, the cured coating has a thickness of at least about 1 micron, and preferably, at least about 2 microns. Typically, the cured coating has a thickness of no greater than about 50 microns, preferably, no greater than about 25 microns, more preferably, no greater than about 10 microns, and most preferably, no greater than about 4 microns. The amount of the ceramer composition applied to the substrate is adjusted to provide this coating thickness.

Once the ceramer composition has formed an adhesion-enhancing coating on the organic polymeric substrate, an optically functional coating can be formed on at least a portion of the adhesion-enhancing coating. As previously mentioned, preferred optically functional coatings are substantially hydrocarbon free and can be formed from one or more thin metal, or metal oxide films. More preferably, the optically functional coating is formed from a material selected from the group of oxides of aluminum, silicon, tin, titanium, niobium, zinc, zirconium, tantalum, yttrium, aluminum, cerium, tungsten, bismuth, indium, and mixtures thereof.

Objects and advantages of this invention will now be illustrated by the following Examples, but the particular materials and amounts thereof recited in these examples, as well as other conditions and details, should not be construed to unduly limit this invention.

Experimental Examples

Advantages of the invention are illustrated by the following examples. However, the particular materials and amounts thereof recited in these examples, as well as other conditions and details, are to be interpreted to apply broadly in the art and should not be construed to unduly limit the invention.

Test Procedure 1 - Dry Adhesion:

This test was run according to ASTM Test Procedure D3359-95 (Standard Test Methods for Measuring Adhesion by Tape Test). This adhesion test was used to determines how well the sputter-deposited metal oxide antireflective film coating adheres to the underlying substrate. The test was carried out using a multiblade cutter commercially available from BYK/Gardner, Inc. of Silver Spring, MD. The cutter had six parallel blades spaced 1.5 mm (0.06 inch) apart. The test specimen was cut in a cross-hatch pattern according to Fig. 1 of ASTM D3359-95. After the cuts were made, the surface was brushed lightly to remove any surface debris.

The adhesion of the coating was tested by gently placing the center of a 2.5 cm wide piece of adhesive tape (SCOTCH Brand Transparent Tape No. 850, commercially available from Minnesota Mining and Manufacturing Company, St. Paul, MN) on the grid, pressing the tape onto the grid by passing a rubber roller weighing 5 pounds (2.3 kg) once over the tape, and then removing the tape at 180 angle at a rapid rate. The grid was examined using an illuminated magnifier and rated according to the classification set forth in ASTM D3359-93. To provide an effective antireflective film for a particular substrate, the sputter deposited metal oxide antireflective coating of this invention must exhibit an adhesion value of 5B on the Gardner scale, which represents no delamination. That is, the edges of the cuts are completely smooth with none of the grid squares detached. A value of 5B is needed to pass this test.

Test Procedure 2 - Knoop Indentation Hardness:

This test was run according to ASTM Test Procedure D1474-85 (Standard Test Methods for Indentation Hardness of Organic Coatings). This method (Method A in ASTM D1474-85) consists of applying a 25-gram load to the surface of a coating by means of a pyramidal shaped diamond having specified face angles, and converting the measurements of the resultant permanent impression to a hardness number expressed as KHN (Knoop Hardness Number). All measurements of KHN were carried out on a Micromet-4 Microhardness Tester (manufactured by Buehler LTD, Lake Bluff, IL). Prior to testing all samples were coated with an extremely thin layer of Palladium/Gold metal for the purpose of enhancing the

contrast between the microindented area and the rest of the flat film. The Palladium/Gold thin film was deposited by sputtering in the vacuum chamber of a Denton Vacuum Model Desk II Cold Sputter/Etch Unit (manufactured by Denton Vacuum, Moorestown, NJ) under the following operating conditions: 50 mTorr vacuum pressure, 30-40 milliamps sputtering current, and 45 seconds sputtering time. In all cases the thickness of the sputter-deposited Palladium/Gold film was found to be in the range 20-30 nanometer and therefore of negligible effect on the indentation hardness of the underlying sample.

Test Procedure 3 - Pencil Hardness:

This test was run according to ASTM D3363-92a (Standard Test Method for Film Hardness by Pencil Test). This test method covers a procedure for rapid determination of the film hardness of an organic coating on a substrate in terms of drawing leads or pencils leads of known hardness. In this test method all test samples were placed on a 1/8 inch (0.3 cm) horizontal glass sheet and the carefully planarized tip (see section 6.1) of a lead pencil of specified hardness held firmly against the film at 45 angle and pushed away from the operator in a 1/4-inch (6.5 mm) stroke. The process is started with the hardest pencil and continued down the scale of hardness to the pencil that will not cut into or gouge the film. Uni Hardness Pencils (manufactured by Mitsubishi, Japan) were used throughout this test.

Test Procedure 4 - Determination of the Optical Clarity:

The relative optical clarity of all samples in the following examples were determined by measuring their haze according to the procedure of ASTM Standard D-1003-95 "Standard Test Method for Haze and Luminous Transmittance of Transparent Plastics," wherein the method recommended in paragraph X2 "Alternative Haze (Short-cut) Procedure" was followed. In this short-cut procedure the observed haze of a sample (that is, the percent of transmitted light that is scattered so that its direction deviates more than a specified angle from the direction of the incident beam) was determined at 23°C using a Pacific Instruments Model XL211 Hazemeter (Gardner Neotec Instrument Division, Silver Springs,

MD) equipped with an integrating sphere. The lower the percent haze value, the higher the optical clarity of the sample under consideration.

Preparation of ceramer composition (A):

In a round-bottomed flask were mixed 1195 grams (g) of NALCO 2327 silica sol (an ammonium ion-stabilized dispersion (40% solids) of colloidal silica particles having a pH of 9.3 and average particle diameter of 20 nanometers, available from Nalco Chemical Co., Chicago, IL), 118 g of N,N-dimethyl acrylamide (Aldrich Chemical Company, Inc.), 120 g of 3-(trimethoxysilyl)propyl methacrylate coupling agent (Aldrich Chemical Company, Inc.) and 761 g of pentaerythritol triacrylate (Aldrich Chemical Company, Inc.).

The round-bottomed flask was then mounted on the vacuum line of a Buchi R152 Rotavapor (Buchi Laboratory AG, Flanil, Switzerland) with the bath temperature set at 55°C. A refrigerated mixture of 50% deionized water/50% antifreeze (Texaco) recirculated through the cooling coils. Volatile components were removed at a reduced pressure of 25 mm Hg until the distillation rate was reduced to less than 5 drops per minute (approximately 2 hours). The resulting material (1464 g) was a clear liquid dispersion of acrylated silica particles in a mixture of N,N-dimethyl acrylamide and pentaerythritol acrylate monomers (a ceramer). The refractive index of this dispersion was 1.5024.

Preparation of ceramer composition (B):

In a glass round-bottom flask were mixed 67.15 g of NALCO 1042 silica sol (an acidic silica sol (34% solids) having a pH = 2.8 and average particle diameter of 20 nanometers, available from Nalco Chemical Co., Chicago, IL), 11.2 g of 2-hydroxyethyl acrylate, 5.6 g of 3-(trimethoxysilyl)propyl methacrylate coupling agent, and 7.9 g of pentaerythritol triacrylate. Water was extracted using a Buchi 121 Rotavapor exactly as in preparation (A). The resulting anhydrous dispersion was crystal clear and almost water-thin.

Preparation of ceramer composition (C):

In a 500 ml round bottom flask were mixed 100 g of NALCO 1042 silica sol (34% solids, pH 3.2, mean particle size 20 nanometer), 2 g of glacial acetic acid catalyst, and 21 g of methyl triethoxysilane (Aldrich Chemical Company, Inc.) and 65 g of reagent grade ethanol. This mixture was stirred vigorously at room

temperature for 24 hours, after which the round bottom flask was attached to a rotovap and the water/alcohol mixture evaporated at 42°C using a Buchi 121 Rotavapor. The viscous, clear, residue in the round bottom flask was then completely redispersed in 65 g of ethanol to give a clear suspension.

Preparation of ceramer composition (D):

In a 500 ml round bottom flask were mixed 100 g of NALCO 1042 silica sol, 3 g of glacial acetic acid and 35 g of Nyacol 50/20 zirconia sol (20% ZrO_2 solids, nitrate stabilized, obtained from Nyacol Corporation, Philadelphia, PA). To this mixed oxide suspension were added dropwise and with vigorous mixing 25 g of phenyl triethoxysilane (Aldrich Chemical Company, Inc.) dissolved in 65 g of ethanol. After mixing for 2 hours at room temperature, the round bottom flask was attached to the rotoevaporator and the water ethanol diluent removed under vacuum at 35°C. The viscous residue in the round bottom flask was then redispersed in 85 g of ethanol to give a stable, bluish-tint suspension.

Preparation of ceramer composition (E):

Ceramer composition (E) is obtained in exactly the same manner as ceramer composition (B) except that no 3-(trimethoxysilyl)propyl methacrylate coupling agent was used.

Comparative Example A

The hardness and optical properties of the substrate, as described above, were determined as follows:

A - Indentation hardness: a 25 mm x 75 mm sample of a substrate (a polyester film having a thickness of about 4-7 mils (0.10-0.18 mm) which included an acrylate-based primer layer commercially available under the trade designation ICI 617 or ICI 505P, from Imperial Chemical Industries, Hopewell, VA) was attached by means of two thin segments of 3M Scotch Double Stick Tape to a 25 x 75 x 2 mm glass microscope slide (VWR Scientific) in such a way that at least 95% of the polyester film rested in direct contact with the hard glass surface. The microscope glass was then placed in the vacuum chamber of a Denton Vacuum Model Desk II Cold Sputter/Etch Unit (Denton Vacuum, Moorestown, NJ 08057) and the polyester side coated with a thin layer of Palladium/Gold according to Test Procedure 2. Knoop hardness at ambient conditions (27% relative humidity, 23°C)

was measured according to Test Procedure 2. The observed average indentation hardness over 3 successive determinations was 19.1 KHN. This result is reported in Table I.

B - Pencil hardness: Samples of the substrate were placed on 1/8 inch (0.3 cm) thick glass plate and their pencil hardness measured as in Test Procedure 3. As reported in Table 1, the average pencil hardness of the polyester film was found to be 2H.

C - Optical clarity: Sheets of uncoated substrate were subjected to Test Procedures 4 above. As seen in Table 1, the percent haze of these film samples was found to be 0.6, indicating excellent optical clarity.

Comparative Example B

A thin film of ITO having a thickness of 130 nanometer was vacuum deposited on the substrate, as described above, using a DC magnetron sputtering apparatus equipped with a 90/10% In_2O_3/SnO_2 target. Throughout the deposition process the vacuum pressure was held at 8.0 mTorr with an oxygen gas flow of 1.6 SCCM (standard cubic centimeter per minute) and an argon gas flow of 30 SCCM. The apparatus was operated at a power setting of 285 watts, a voltage of 349 volts and a current of 0.8 amperes. The polyester substrate was supported on a coating web moving at a constant speed of 4 inches per minute (10.2 cm/minute).

Samples of the ITO-coated substrate were conditioned for 24 hours at the ambient environment (53% relative humidity and 23°C) and then subjected to Test Procedures 1, 2, 3, and 4 above. It is seen from Table 1 that the sputter-deposited ITO thin film did not adhere to the underlying polyester substrate as it completely failed the cross-hatch adhesion test. On the other hand, the indentation hardness, pencil hardness and optical clarity of the ITO coated polyester were indistinguishable from those of bare polyester observed in Comparative Example A.

Example 1

An improved substrate obtained by overcoating the substrate, as described above, with a ceramer composition was prepared as follows: 4 parts of Ceramer composition (A) were added to 21 parts isopropanol and 0.14 part of IRGACURE

184 photoinitiator to form a 16 wt.% clear, crosslinkable ceramer dispersion in isopropanol. This 16 wt.% dispersion was coated onto polyester substrate (as described in Comparative Example A) using a #21 wire-bound coating bar (available from RD Specialties, Rochester, NY). Immediately after coating, the coated sheets were placed in a forced air convection oven for 2.5 minutes at 67°C to flash off the isopropanol. Next, the coated sheets were placed onto the conveyor belt of a UV Curing Station (Model MC-6RQN, Fusion UV curing Inc., Rockville, MD) equipped with a Fusion "H" lamp, and running at a belt speed of 30 feet/minute (9 meters/minute). The resulting cured coatings on the substrate were perfectly clear to the eye. They were about 3.0-3.5 microns thick. The average percent haze of the coated sheets, measured according to Test Procedure 4 was 0.7%.

Samples of the cured coating were additionally subjected to Test Procedures 2 and 3. It is seen from Table 1 that the Knoop hardness of the ceramer is at least twice the value for bare polyester observed in Comparative Example A. Similarly, the pencil hardness of the ceramer is five fold higher than that of the bare polyester of Comparative Example A.

Example 2

Sheet samples (7.5 cm x 7.5 cm) of ceramer-coated substrate prepared in Example 1 were introduced into the vacuum chamber of the sputter-deposition apparatus and an ITO thin film 130 nanometer thick was deposited on the ceramer surface under exactly the same conditions as described in Comparative Example B.

The resulting ITO coated samples were conditioned for 24 hours at the ambient environment (53% relative humidity and 23°C) and then subjected to Test Procedures 1, 2, 3, and 4 above. It is seen from Table 1 that the sputter-deposited ITO thin film exhibited 100 percent cross-hatch adhesion to the ceramer coated polyester, unlike the case of the ITO film deposited directly on polyester in Example 2. Moreover, it is seen from Table 1 that both the Knoop indentation hardness and pencil hardness are several folds higher than those of Example 2, indicating that the ceramer interlayer derived from composition (A) between the polyester film substrate and the ITO thin film has a profound effect on the durability of the sputter-deposited metal oxide thin film.

Comparative Example C

The hardness and optical properties of a typical acrylic substrate used as the organic substrate in antireflective film constructions were determined as follows:

A - Indentation hardness: Square samples of 3 mm thick unprimed acrylic substrates (commercially available under the trade designation ACRYLITE, from Cyro Industries, Woodcliff Lake, NJ) were coated with Palladium/Gold and their Knoop indentation hardness determined as in Test Procedure 2. The average Knoop hardness observed over three samples was found to be 19.0 as shown in Table 1.

B - Pencil hardness: Samples of the above acrylic sheets were tested for their pencil hardness according to Test Procedure 3. As reported in Table 1, the average pencil hardness of the acrylic sheets was found to be 1H.

C - Optical clarity: Samples of the above acrylic sheets were subjected to Test Procedure 4 above. As seen in Table 1, the percent haze of these sheets was found to be 0.6, indicating excellent optical clarity.

Comparative Example D

A thin film of ITO having a thickness of 130 nanometer was vacuum deposited on the acrylic sheets of Comparative Example C using exactly the same conditions as in Comparative Example B.

Samples of the ITO-coated acrylic sheets were conditioned for 24 hours at the ambient environment and then subjected to Test Procedures 1,2,3 and 4 above. The results are reported in Table 1. It is seen from the Table that the sputter-deposited ITO thin film exhibited 0% adhesion to the acrylic substrate. The Knoop indentation hardness, pencil hardness and optical clarity of the ITO coated acrylic were indistinguishable from those of the bare polyester sheets in Comparative Example A.

Example 3

Sheets of unprimed acrylic from Comparative Example C (ACRYLITE, obtained from Cyro Industries, Woodcliff Lake, NJ) were overcoated with a ceramer coating prepared and cured exactly as in Example 1. The surface and optical properties of the ceramer coated acrylic sheets were then determined according to Test Procedures 2, 3, and 4. The results are reported in Table 1. It is

seen from this Table that the Knoop indentation hardness of the ceramer coated acrylic (50) is more than twice as high as the Knoop hardness of the bare acrylic substrate (19.0) of Example 5. Moreover, the pencil hardness of the ceramer coated acrylic is five fold greater than the pencil hardness of the bare acrylic of Comparative Example C, while the optical clarity for both the ceramer coated acrylic and the bare acrylic sheets are virtually identical.

Example 4

Square samples (7.5 cm x 7.5 cm) of ceramer-coated acrylic sheets prepared in Example 3 were introduced into the vacuum chamber of the sputter-deposition apparatus and an ITO thin film, 130 nanometer thick, was deposited on the ceramer surface under exactly the same conditions as described in Comparative Example B.

Samples of the ITO-coated acrylic substrate were conditioned for 24 hours at the ambient environment (53% relative humidity and 23°C) and then subjected to Test Procedures 1, 2, 3, and 4 above. It is seen from Table 1 that the sputter-deposited ITO thin film exhibited 100 percent cross-hatch adhesion to the ceramer coated acrylic, unlike the case of the ITO film deposited directly on acrylic in Comparative Example D. Moreover, it is seen from Table 1 that both the Knoop indentation hardness and pencil hardness are several folds higher than those of Comparative Example D, indicating that the ceramer interlayer between the acrylic film substrate and the ITO thin film has a profound effect on the durability of the sputter-deposited metal oxide thin film.

Comparative Example E

Comparative Example A was repeated, except that instead of a polyester film a polycarbonate film (175 microns thick, obtained from Tekra Corporation, New Berlin, WI) was used as the organic substrate. The observed Knoop hardness of this polycarbonate was 17.1. Its pencil hardness was 1H and its percent haze was 0.9.

Comparative Example F

A thin film of ITO having a thickness of 130 nanometer was vacuum deposited on the polycarbonate film of Comparative Example E using exactly the same procedure as in Comparative Example B.

Samples of the ITO-coated polycarbonate film were conditioned for 24 hours at the ambient environment and then subjected to Test Procedures 1, 2, 3, and 4 above. It was found that the sputter-deposited ITO thin film did not adhere to the underlying polycarbonate substrate as it completely failed the cross-hatch adhesion test (see Table 1). The Knoop indentation hardness, pencil hardness and optical clarity of the ITO coated polycarbonate were indistinguishable from those of bare polycarbonate observed in Comparative Example E.

Example 5

An improved substrate obtained by overcoating the polycarbonate substrate of Comparative Example E with a ceramer coating was prepared as follows: 4 parts of Ceramer composition (A) were added to 21 parts isopropanol and 0.14 part of IRGACURE 184 photoinitiator to form a 16 wt.% clear, crosslinkable ceramer dispersion in isopropanol. This 16 wt.% dispersion was coated, dried and cured onto samples of the polycarbonate film of Comparative Example E in exactly the same manner described in Example 1. The resulting cured coatings on the polycarbonate substrate were perfectly clear to the eye. The average percent haze of the coated sheets, measured according to Test Procedure 4 was 1.1, indicating excellent optical clarity.

The face of the polycarbonate film bearing the cured ceramer coating was additionally subjected to Test Procedures 2 and 3. It is seen from Table 1 that the Knoop hardness of the ceramer is more than twice the value for bare polycarbonate observed in Comparative Example E. Similarly, the pencil hardness of the ceramer is five fold higher than that of the bare polycarbonate of Comparative Example E.

Example 6

A thin film of ITO having a thickness of 130 nanometer was vacuum deposited on the polycarbonate film of Example 5 using exactly the same procedure as in Comparative Example B.

Samples of the ITO-coated polycarbonate film were conditioned for 24 hours at the ambient environment (53% relative humidity and 23°C) and then subjected to Test Procedures 1, 2, 3, and 4 above. The results, displayed in Table 1, indicate that the sputter-deposited ITO thin film exhibited 100 percent cross-hatch adhesion to the ceramer coated polycarbonate, unlike the case of the ITO film

deposited directly onto polycarbonate as in Comparative Example F. Moreover, it is seen from Table 1 that both the Knoop indentation hardness and pencil hardness are several folds higher than those of Comparative Example F, indicating that the ceramer interlayer between the polycarbonate film substrate and the ITO thin film has a profound effect on the durability of the sputter-deposited metal oxide thin film.

Example 7

An improved substrate obtained by overcoating the polyester film of Comparative Example A with a ceramer coating was prepared as follows: 4 g of Ceramer composition (B) were added to 21 g of isopropyl alcohol and 0.14 g of IRGACURE 184 photoinitiator to give a 16 wt.% dispersion in the solvent. This 16 wt.% dispersion was coated on the polyester substrate of Comparative Example A and subsequently cured in exactly the same fashion as in Example 1. The resulting cured coating on the polyester sheets was optically clear to the naked eye. The average percent haze of the coated sheets was 0.7.

Samples of the cured coating were additionally subjected to Test Procedures 2 and 3. It is seen from Table 1 that the Knoop hardness of the ceramer is at least twice the value for bare polyester observed in Comparative Example A. Similarly, the pencil hardness of the ceramer is five fold higher than that of the bare polyester of Comparative Example A.

Example 8

Sheet samples (7.5 cm x 7.5 cm) of ceramer-coated polyester film prepared in Example 7 were introduced into the vacuum chamber of the sputter-deposition apparatus and an ITO thin film 130 nanometer thick was deposited on the ceramer surface under exactly the same conditions as described in Comparative Example B. The resulting ITO coated samples were conditioned at the ambient environment for at least 24 hours and then subjected to Test Procedures 1, 2, 3, and 4. The sputter-deposited ITO thin film exhibited 100 percent cross-hatch adhesion to the ceramer coated polyester, unlike the case of the ITO film deposited directly onto polyester in Comparative Example B. Furthermore, it is seen from Table 1 that both the Knoop indentation hardness and pencil hardness are several folds higher than those of Comparative Example B, indicating that the ceramer interlayer derived from

composition (B) between the polyester film substrate and the ITO thin film has a profound effect on the durability of the sputter-deposited metal oxide thin film.

Comparative Example G

This example evaluates a crosslinked organic polymer filled with colloidal silica powder (fumed silica) that has been surface treated with a coupling agent.

A mixture containing 50 parts fumed silica powder (AEROSIL R972, available from DeGussa Corp., Teterboro, NJ), 2.5 parts 3-(trimethoxysilyl)propyl methacrylate coupling agent (Aldrich Chemical Company, Inc., Milwaukee, WI), 7.5 parts deionized water and 50 parts pentaerythritol triacrylate was homogenized in a high shear mixer for 30 minutes. Four grams of this homogenized composition were added to 21 g of isopropyl alcohol and 0.14 g of IRGACURE 184 photoinitiator to give a 16 wt.% dispersion in the water/alcohol mixture. This 16 wt.% dispersion was coated on the polyester substrate of Comparative Example A and subsequently cured in exactly the same fashion as in Example 1. The resulting cured coating on the polyester sheets was not optically clear. The average percent haze of the coated sheets was 40, rendering this coating unsuitable as a substrate for antireflective constructions.

Example 9

An improved antireflective construction using a ceramer coating derived from composition (C) was obtained as follows: In a first step, square samples of acrylic sheets as in Comparative Example C were flow-coated with ceramer composition (C) using a disposable polyethylene syringe fitted with a Gelman Acrodisc disposable filter (0.45 micron nominal porosity). The coated sheets were left at room temperature for 12 minutes and then baked at 95°C for 2 hours to effectuate cure of the ceramer coating. The resulting coat was crystal clear.

In a second step, a thin film of ITO having a thickness of 130 nanometers was vacuum deposited on the ceramer coated acrylic sheets using exactly the same conditions as in Comparative Example B. Samples of the ITO-coated acrylic were conditioned for 24 hours at the ambient environment (53% relative humidity and 23°C) and then subjected to Test Procedures 1, 2, 3, and 4 above.

It is seen from Table 1 that the sputter-deposited ITO thin film exhibited 100 percent cross-hatch adhesion to the ceramer coated acrylic, unlike the case of

the ITO film deposited directly on acrylic in Comparative Example D. Moreover, it is seen from Table 1 that both the Knoop hardness and pencil hardness are several folds higher than those of Comparative Example D, indicating that the ceramer interlayer between the acrylic substrate and the ITO thin film has a profound effect on the durability of the sputter-deposited metal oxide thin film.

Example 10

An improved antireflective construction using a ceramer hardcoat derived from composition (D) was obtained as follows: The two-step procedure in Example 9 was repeated except that in the first step the acrylic sheets were coated with composition (D) instead of composition (C). Here again, it is seen from Table 1 that the sputter-deposited ITO thin film exhibited 100 percent cross-hatch adhesion to the ceramer coated acrylic, unlike the case of the ITO film deposited directly on acrylic in Comparative Example D. Moreover, it is seen from Table 1 that both the Knoop hardness and pencil hardness are several folds higher than those of Comparative Example D, indicating that the ceramer interlayer containing both SiO_2 and ZrO_2 between the acrylic substrate and the ITO thin film enhances by several folds the scratch resistance and overall durability of the sputter-deposited metal oxide thin film.

Example 11

An improved substrate obtained by overcoating the polyester film of Comparative Example A with a ceramer coating was prepared as follows: 4 g of Ceramer composition (E) were added to 21 g of isopropyl alcohol and 0.14 g of IRGACURE 184 photoinitiator to give a 16 wt.% dispersion in the solvent. This 16 wt.% dispersion was coated on the polyester substrate of Comparative Example A and subsequently cured in exactly the same fashion as in Example 1. The resulting cured coating on the polyester sheets was optically clear to the naked eye. The average percent haze of the coated sheets was 0.7.

Samples of the cured coating were additionally subjected to Test Procedures 2 and 3. It is seen from Table 1 that the Knoop hardness of the ceramer is at least twice the value for bare polyester observed in Comparative Example A. Similarly, the pencil hardness of the ceramer is five fold higher than that of the bare polyester of Comparative Example A.

Example 12

Sheet samples (7.5 cm x 7.5 cm) of ceramer-coated polyester film prepared in Example 11 were introduced into the vacuum chamber of the sputter-deposition apparatus and an ITO thin film 130 nanometer thick was deposited on the ceramer surface under exactly the same conditions as described in Comparative Example B. The resulting ITO coated samples were conditioned at the ambient environment for at least 24 hours and then subjected to Test Procedures 1, 2, 3, and 4. The sputter-deposited ITO thin film exhibited 100 percent cross-hatch adhesion to the ceramer coated polyester, unlike the case of the ITO film deposited directly onto polyester in Comparative Example B. Furthermore, it is seen from Table 1 that both the Knoop indentation hardness and pencil hardness are several folds higher than those of Comparative Example B, indicating that the ceramer interlayer derived from composition (E) between the polyester film substrate and the ITO thin film has a profound effect on the durability of the sputter-deposited metal oxide thin film.

Table 1

Example	Dry Adhesion	Knoop Hardness (KHN)	Pencil Hardness	Optical Clarity
Comp. Ex. A	-	19.1	1H	0.6
Comp. Ex. B	0B	19.1	1H	0.6
1		49.9	5H	0.7
2	5B	49.9	5H	0.7
Comp. Ex. C	-	19	1H	0.5
Comp. Ex. D	0B	19	1H	0.5
3	-	50.0	5H	0.5
4	5B	50.0	5H	0.5
Comp. Ex. E	-	17.1	1H	0.9
Comp. Ex. F	0B	17.1	1H	0.9
5	-	50.1	5H	1.1
6	5B	50.1	5H	0.9
7		44.4	5H	0.7

Example	Dry Adhesion	Knoop Hardness (KHN)	Pencil Hardness	Optical Clarity
8	5B	44.6	5H	0.7
Comp. Ex. G	-	-	-	40
9	5B	41	5H	0.6
10	5B	45	5H	0.9
11	-	45	5H	0.7
12	5B	45	5H	0.8

The foregoing detailed description and examples have been given for clarity of understanding only. No unnecessary limitations are to be understood therefrom. The invention is not limited to the exact details shown and described, for variations obvious to one skilled in the art will be included within the invention defined by the claims.

WHAT IS CLAIMED IS:

1. A composite structure comprising:

an organic polymeric substrate having a first surface and a second surface;

an adhesion-enhancing coating on the first surface, wherein the coating comprises an organic matrix having inorganic oxide particles dispersed therein; wherein the organic matrix comprises at least one polymerized ethylenically unsaturated monomer and the inorganic oxide particles comprise silica particles; and

an optically functional coating on the adhesion-enhancing coating.

2. An antireflective composite structure comprising:

an organic polymeric substrate having a first surface and a second surface;

an adhesion-enhancing coating on the first surface, wherein the coating comprises an organic matrix and inorganic colloidal particles that at least include silica dispersed in the organic matrix; and

an antireflective coating on the adhesion-enhancing coating, wherein the antireflective coating comprises at least one film comprising a material selected from the group of oxides of aluminum, silicon, tin, titanium, niobium, zinc, zirconium, tantalum, yttrium, aluminum, cerium, tungsten, bismuth, indium, and mixtures thereof.

3. An antireflective composite structure comprising:

an organic polymeric substrate having a first surface and a second surface;

an adhesion-enhancing coating on the first surface, wherein the coating comprises an organic matrix and inorganic colloidal particles that at least include silica dispersed in the organic matrix; and

an antireflective coating on the adhesion-enhancing coating, wherein the antireflective coating is substantially hydrocarbon free.

4. An optically functional structure comprising:

an organic polymeric substrate having a first surface and a second surface;

an adhesion-enhancing coating on the first surface, wherein the coating comprises an organic matrix and inorganic colloidal particles that at least include silica dispersed in the organic matrix; wherein the organic matrix is formed from an adhesion-enhancing precursor composition comprising a ceramer composition comprising an organofunctional silane monomer coupling agent, and colloidal inorganic oxide particles that at least include silica; and

an optically functional coating on the adhesion-enhancing coating, wherein the optically functional coating is substantially carbon free.

5. The composite structure of claim 2, wherein the antireflective coating has a refractive index of about 1.45 to about 1.70.

6. The composite structure of claim 1, wherein the adhesion-enhancing coating is prepared from a ceramer composition comprising at least one ethylenically unsaturated monomer and colloidal inorganic oxide particles that include at least silica particles.

7. The antireflective composite structure of claim 2, wherein the adhesion-enhancing coating is prepared from an adhesion-enhancing precursor composition comprising a ceramer composition comprising at least one ethylenically unsaturated monomer, an organofunctional silane monomer coupling agent, and colloidal inorganic oxide particles that include at least silica particles.

8. The composite structure of any one of claims 6 or 7, wherein the ceramer composition has a refractive index of about 1.40 to about 1.65.

9. The optically functional structure of claim 4, wherein the ceramer composition has a refractive index of about 1.40 to about 1.65.

10. The composite structure of claim 1, wherein the optically functional material comprises a layer of indium tin oxide directly on the adhesion-enhancing coating.

11. The composite structure of any one of claims 1, 2, 3, 4, 5, 6, 7, 9, or 10, wherein the organic polymeric substrate is formed from a polymer selected from the group of a polyester, a polycarbonate, a poly(meth)acrylate, a polystyrene, a styrene copolymer, a polyphenyleneoxide, a cellulose ester, a polyolefin, a polyimide, a polyvinyl chloride, and mixtures thereof.

12. A method of forming a composite structure comprising:

providing an organic polymeric substrate having a first surface and a second surface;

coating an adhesion-enhancing precursor composition on the first surface of the substrate, wherein the adhesion-enhancing precursor composition comprises a ceramer composition comprising at least one ethylenically unsaturated monomer and colloidal inorganic silica particles;

at least partially curing the adhesion-enhancing precursor composition to form an adhesion-enhancing coating; and

forming an optically functional coating on the adhesion-enhancing coating.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 98/11135

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 G02B1/11 G02B1/10

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 G02B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 96 23243 A (ESSILOR INT) 1 August 1996 see page 4, line 14 - page 6, line 5; example 2 ---	1-9,11, 12
X	PATENT ABSTRACTS OF JAPAN vol. 015, no. 372 (P-1254), 19 September 1991 & JP 03 145602 A (SEIKO EPSON CORP;OTHERS: 01), 20 June 1991 see abstract ---	1-3,12

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[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

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"P" document published prior to the international filing date but later than the priority date claimed

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Date of the actual completion of the international search	Date of mailing of the international search report
23 September 1998	01/10/1998

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	von Moers, F

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INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 98/11135

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication,where appropriate, of the relevant passages	Relevant to claim No.
X	DATABASE WPI Section Ch, Week 9704 Derwent Publications Ltd., London, GB; Class A14, AN 97-038134 XP002078488 & JP 08 295846 A (SEIKO EPSON CORP) , 12 November 1996 see abstract ---	1
X	DATABASE WPI Section Ch, Week 8540 Derwent Publications Ltd., London, GB; Class A28, AN 85-246682 XP002078489 & JP 60 163001 A (ASAHI GLASS CO LTD) , 24 August 1985 see abstract ---	2
A	DATABASE WPI Section Ch, Week 8617 Derwent Publications Ltd., London, GB; Class A85, AN 86-109331 XP002078490 & JP 61 051101 A (TORAY IND INC) , 13 March 1986 see abstract -----	10

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INTERNATIONAL SEARCH REPORT

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